

What is claimed is:

1. A method for coating a porous polyurethane resin with an aromatic isocyanate coating composition comprising the steps of:

(a) providing a porous polyurethane resin substrate comprising at least one surface upon which the coating composition is to be applied;

10

(b) applying one or more primary layers to said substrate surface, said primary layer comprising an aqueous solution of a compound that includes at least one -OH reactive group in its non-aqueous, dry state, which is capable, upon drying, of forming a self-supporting, continuous film on said substrate surface at room temperature;

15

(c) optionally subjecting the applied primary layer to forced drying conditions at a temperature below the softening point of said porous polyurethane resin; and

20

(d) after allowing the primary layer to substantially dry, applying a secondary layer to the primary layer, said secondary layer comprising an aromatic isocyanate compound containing one or more reactive -NCO groups for reaction with the -OH reactive group in the primary layer;

25

wherein a continuous, film-forming coating is formed on said substrate surface.

30

2. The method according to claim 1 wherein multiple

coatings of the primary layer are applied to said substrate surface.

3. The method according to claim 1 wherein the primary
5 layer comprises an aqueous solution of polyvinyl alcohol or polyvinyl alcohol/polyvinyl acetate copolymer, the polyvinyl acetate component of the copolymer being present in an amount of 1-14 weight percent.

10 4. The method according to claim 3 wherein the concentration of the polyvinyl alcohol or polyvinyl alcohol/polyvinyl acetate copolymer solution is about 0.5 to 5.0 percent by weight.

15 5. The method according to claim 1 wherein the primary layer comprises an aqueous solution of carboxymethylcellulose.

20 6. The method according to claim 5 wherein the concentration of the carboxymethylcellulose solution is about 1 to 3 percent by weight.

25 7. The method according to claim 5 wherein the concentration of the carboxymethylcellulose solution is about 1.8 to 2.2 percent by weight.

8. The method according to claim 1 wherein the primary layer comprises an aqueous solution of starch.

30 9. The method according to claim 8 wherein the concentration of the starch solution is about 1 to 8 percent by weight.

10. The method according to claim 9 wherein the concentration of the starch solution is about 3 to 5 percent by weight.

5 11. The method according to claim 1 wherein the primary layer comprises an aqueous solution of sodium or ammonium polyacrylate.

10 12. The method according to claim 11 wherein the concentration of the sodium or ammonium polyacrylate solution is about 10 to 51 percent by weight and the sodium or ammonium polyacrylate has a molecular weight range of about 2,000 to 6,000.

15 13. The method according to claim 12 wherein the concentration of the sodium or ammonium polyacrylate solution is about 20 to 41 percent by weight.

20 14. The method according to claim 1 wherein the primary layer comprises an aqueous solution of polyacrylic acid.

25 15. The method according to claim 14 wherein the concentration of the polyacrylic acid solution is about 10 to 41 percent by weight and the polyacrylic acid has a molecular weight range of about 2,000 to 6,000.

30 16. The method according to claim 15 wherein the concentration of the polyacrylic acid solution is about 20 to 41 percent by weight.

17. The method according to claim 1 wherein the

primary layer comprises an aqueous solution of sodium polycarboxylate.

5 18. The method according to claim 17 wherein the concentration of the sodium polycarboxylate solution is about 10 to 41 percent by weight and the sodium polycarboxylate has a molecular weight range of about 2,000 to 170,000.

10 19. The method according to claim 18 wherein the concentration of the sodium polycarboxylate solution is about 20 to 41 percent by weight.

15 20. The method according to claim 1 wherein the primary layer comprises an aqueous solution of an alkyl acrylate or alkyl methacrylate compound.

20 21. The method according to claim 20 wherein the concentration of the alkyl acrylate or alkyl methacrylate solution is about 5 to 40 percent by weight and the alkyl acrylate or alkyl methacrylate has a molecular weight range of about 5,000 to 10,000.

25 22. The method according to claim 21 wherein the concentration of the alkyl acrylate or alkyl methacrylate solution is about 10 to 20 percent by weight.

30 23. The method according to claim 1 wherein the primary layer comprises an aqueous solution of gum arabic.

24. The method according to claim 23 wherein the concentration of the gum arabic solution is about 5 to 40

percent by weight.

25. The method according to claim 1 wherein the aromatic isocyanate coating composition is in the form of a water-based, polyurethane paint.

26. The method according to claim 1 wherein the aromatic isocyanate coating composition is in the form of a solvent-based, polyurethane paint.

10

27. The method according to claim 1 wherein the porous polyurethane resin has a density in the range of about 0.002 to 1.000 kilograms per cubic meter.

15

28. A method for preparing a reactive film-forming surface on a porous polyurethane substrate for bonding with a coating composition comprising an aromatic isocyanate compound, comprising the steps of

20

(a) providing a porous polyurethane substrate comprising a density of from about 0.002 to about 1.000 kilograms/cubic meter and at least one surface for preparing the reactive film-forming surface thereon;

25

(b) applying to the surface of the porous polyurethane substrate, at least one layer comprising an aqueous solution of a compound that includes at least one -OH reactive group in its non-aqueous, dry state, said layer being capable, upon drying, of forming a self-supporting, continuous film on said substrate surface at room temperature; and

30

(c) optionally subjecting the layer to forced drying conditions at a temperature below the softening temperature of the substrate.

5 29. The method according to claim 28 wherein more than one layer of the aqueous solution is applied to said substrate surface.

10 30. The method according to claim 28 wherein the layer comprises an aqueous solution of polyvinyl alcohol or polyvinyl alcohol/polyvinyl acetate copolymer, the polyvinyl acetate component of the copolymer being present in an amount of 1-14 weight percent.

15 31. The method according to claim 30 wherein the aqueous concentration of the polyvinyl alcohol or polyvinyl alcohol/polyvinyl acetate copolymer is about 0.5 to 5.0 percent by weight.

20 32. The method according to claim 28 wherein the layer comprises an aqueous solution of carboxymethylcellulose.

25 33. The method according to claim 32 wherein the aqueous concentration of the carboxymethylcellulose solution is about 1 to 3 percent by weight.

30 34. The method according to claim 32 wherein the aqueous concentration of the carboxymethylcellulose solution is about 1.8 to 2.2 percent by weight.

 35. The method according to claim 28 wherein the layer comprises an aqueous solution of starch.

36. The method according to claim 35 wherein the aqueous concentration of the starch solution is about 1 to 8 percent by weight.

5 37. The method according to claim 35 wherein the aqueous concentration of the starch solution is about 3 to 5 percent by weight.

10 38. The method according to claim 28 wherein the layer comprises an aqueous solution of sodium or ammonium polyacrylate.

15 39. The method according to claim 38 wherein the concentration of the sodium or ammonium polyacrylate solution is about 10 5 to 51 percent by weight and the molecular weight range of the sodium or ammonium polyacrylate is about 2,000 to 10,000.

20 40. The method according to claim 39 wherein the concentration of the sodium or ammonium polyacrylate solution is about 20 to 41 percent by weight.

25 41. The method according to claim 28 wherein the layer comprises an aqueous solution of polyacrylic acid.

30 42. The method according to claim 41 wherein the concentration of the polyacrylic acid solution is about 5 to 41 percent by weight and the molecular weight range of the polyacrylic acid is about 2,000 to 170,000.

43. The method according to claim 42 wherein the concentration of the polyacrylic acid is about 20 to 41

percent by weight.

44. The method according to claim 28 wherein the layer comprises an aqueous solution of sodium polycarboxylate.

5

45. The method according to claim 44 wherein the concentration of the sodium polycarboxylate solution is about 10 to 41 percent by weight and the molecular weight range of the sodium polycarboxylate is about 2,000 to 170,000.

10

46. The method according to claim 45 wherein the concentration of the sodium polycarboxylate solution is about 20 to 41 percent by weight.

15

47. The method according to claim 28 wherein the layer comprises an aqueous solution of an alkyl acrylate or alkyl methacrylate compound.

20

48. The method according to claim 47 wherein the concentration of the alkyl acrylate or alkyl methacrylate solution is about 5 to 40 percent by weight and the molecular weight range of the alkyl acrylate or alkyl methacrylate compound is about 5,000 to 10,000.

25

49. The method according to claim 48 wherein the concentration of the alkyl acrylate or alkyl methacrylate solution is about 10 to 20 percent by weight.

30

50. The method according to claim 28 wherein the layer comprises an aqueous solution of gum arabic.

51. The method according to claim 50 wherein the concentration of the gum arabic solution is about 5 to 40 percent by weight.

5 52. A porous polyurethane product comprising:

(a) a porous polyurethane resin substrate having a density of from 0.002 to 1.000 kilograms/cubic meter; and

10 (b) at least one coating disposed on at least one surface of said resin substrate, said coating comprising

15 (i) a primary layer comprising an aqueous solution of a primary layer compound that includes at least one -OH reactive group in its non-aqueous, dry state, said primary layer being capable, upon drying, of forming a self-supporting, continuous film on said substrate surface at room temperature; and

20 (ii) a secondary layer overlying said primary layer, said secondary layer comprising an aromatic isocyanate compound that includes at least one -NCO reactive group;

25 wherein the -NCO group of the secondary layer is reacted with the -OH group of the primary layer compound to form a continuous, film-forming coating on said substrate.

30 53. The product according to claim 52 wherein multiple coatings of the primary layer are disposed on said substrate surface.

54. The product according to claim 52 wherein the primary layer comprises an aqueous solution of polyvinyl alcohol or polyvinyl alcohol/polyvinyl acetate copolymer.

5 55. The product according to claim 54 wherein the concentration of the polyvinyl alcohol or polyvinyl alcohol/polyvinyl acetate copolymer solution is about 0.5 to 5.0 percent by weight.

10 56. The product according to claim 55 wherein the polyvinyl acetate component of the copolymer is present in an amount of 1-14 weight percent based on the total weight of the polyvinyl alcohol/polyvinyl acetate copolymer.

15 57. The product according to claim 55 wherein the polyvinyl acetate component of the polyvinyl alcohol/polyvinyl acetate copolymer is present in an amount of 1-2 percent by weight.

20 58. The product according to claim 52 wherein the primary layer comprises an aqueous solution of carboxymethylcellulose.

25 59. The product according to claim 58 wherein the concentration of the carboxymethylcellulose solution is about 1 to 3 percent by weight.

30 60. The product according to claim 58 wherein the concentration of the carboxymethylcellulose solution is about 1.8 to 2.2 percent by weight.

61. The product according to claim 52 wherein the

primary layer comprises an aqueous solution of starch.

62. The product according to claim 61 wherein the concentration of the starch solution is about 1 to 8
5 percent by weight.

63. The product according to claim 61 wherein the concentration of the starch solution is about 3 to 5
10 percent by weight.

64. The product according to claim 52 wherein the primary layer comprises an aqueous solution of sodium or ammonium polyacrylate.

65. The product according to claim 64 wherein the concentration of the sodium or ammonium polyacrylate solution is about 5 to 51 percent by weight and the sodium or ammonium polyacrylate has a molecular weight range of about 2,000 to 10,000.
15

66. The product according to claim 65 wherein the concentration of the sodium or ammonium polyacrylate solution is about 20 to 41 percent by weight.
20

67. The product according to claim 52 wherein the primary layer comprises an aqueous solution of polyacrylic acid.
25

68. The product according to claim 67 wherein the concentration of the polyacrylic acid solution is about 5 to 41 percent by weight and the polyacrylic acid has a molecular weight range of about 2,000 to 170,000.
30

69. The product according to claim 68 wherein the concentration of the polyacrylic acid solution is about 20 to 41 percent by weight.

5

70. The product according to claim 52 wherein the primary layer comprises an aqueous solution of sodium polycarboxylate.

10

71. The product according to claim 70 wherein the concentration of the sodium polycarboxylate solution is about 10 to 41 percent by weight and the sodium polycarboxylate has a molecular weight range of about 2,000 to 170,000.

15

72. The product according to claim 71 wherein the concentration of the sodium polycarboxylate solution is about 20 to 41 percent by weight.

20

73. The product according to claim 52 wherein the primary layer comprises an aqueous solution of an alkyl acrylate or alkyl methacrylate compound.

25

74. The product according to claim 73 wherein the concentration of the alkyl acrylate or alkyl methacrylate solution is about 5 to 40 percent by weight and the alkyl acrylate or alkyl methacrylate has a molecular weight range of about 5,000 to 10,000.

30

75. The product according to claim 74 wherein the concentration of the alkyl acrylate or alkyl methacrylate solution is about 10 to 20 percent by weight.

76. The product according to claim 52 wherein the primary layer comprises an aqueous solution of gum arabic.

5 77. The product according to claim 76 wherein the concentration of the gum arabic solution is about 5 to 40 percent by weight.

10 78. A porous polyurethane product comprising:

(i) a porous polyurethane resin substrate having a density of from about 0.002 to 1.000 kilograms/cubic meter; and

(ii) at least one reactive film-forming layer disposed on at least one surface of said substrate for receiving thereon and reacting with one or more NCO reactive groups of an aromatic isocyanate, film-forming compound, said film-forming layer comprising an aqueous solution of a compound that includes at least one -OH reactive group in its non-aqueous, dry state, said film-forming layer being capable, upon drying, of forming a self-supporting, continuous film on the surface of said substrate at room temperature.

25 79. The product according to claim 78 wherein more than one coating of the film-forming layer is disposed on said substrate surface.

30 80. The product according to claim 79 wherein the film-forming layer comprises an aqueous solution of polyvinyl alcohol or polyvinyl alcohol/polyvinyl acetate copolymer, the polyvinyl acetate component of the copolymer

being present in an amount of 1-14 weight percent.

81. The product according to claim 80 wherein the concentration of the polyvinyl alcohol or polyvinyl alcohol/polyvinyl acetate copolymer solution is about 0.5 to 5.0 percent by weight.

82. The product according to claim 78 wherein the film-forming layer comprises an aqueous solution of carboxymethylcellulose.

83. The product according to claim 82 wherein the concentration of the carboxymethylcellulose solution is about 1 to 3 percent by weight.

84. The product according to claim 82 wherein the concentration of the carboxymethylcellulose solution is about 1.8 to 2.2 percent by weight.

85. The product according to claim 78 wherein the film-forming layer comprises an aqueous solution of starch.

86. The product according to claim 85 wherein the concentration of the starch solution is about 1 to 8 percent by weight.

87. The product according to claim 85 wherein the concentration of the starch solution is about 3 to 5 percent by weight.

88. The product according to claim 78 wherein the film-forming layer comprises an aqueous solution of sodium

or ammonium polyacrylate.

89. The product according to claim 88 wherein the concentration of the sodium or ammonium polyacrylate solution is about 5 to 51 percent by weight and the sodium or ammonium polyacrylate has a molecular weight range of about 2,000 to 10,000.

90. The product according to claim 89 wherein the concentration of the sodium or ammonium polyacrylate solution is about 20 to 41 percent by weight.

91. The product according to claim 78 wherein the film-forming layer comprises an aqueous solution of polyacrylic acid.

92. The product according to claim 91 wherein the concentration of the polyacrylic acid solution is about 5 to 41 percent by weight and the polyacrylic acid has a molecular weight range of about 2,000 to 170,000.

93. The product according to claim 92 wherein the concentration of the polyacrylic acid is about 20 to 41 percent by weight.

94. The product according to claim 78 wherein the film-forming layer comprises an aqueous solution of sodium polycarboxylate.

95. The product according to claim 94 wherein the concentration of the sodium polycarboxylate solution is about 10 to 41 percent by weight and the sodium

polycarboxylate has a molecular weight range of about 2,000 to 170,000.

5 96. The product according to claim 95 wherein the concentration of the sodium polycarboxylate solution is about 20 to 41 percent by weight.

10 97. The product according to claim 78 wherein the primary layer comprises an aqueous solution of an alkyl acrylate or alkyl methacrylate compound.

15 98. The product according to claim 97 wherein the concentration of the alkyl acrylate or alkyl methacrylate solution is about 5 to 40 percent by weight and the alkyl acrylate or alkyl methacrylate has a molecular weight range of about 5,000 to 10,000.

20 99. The product according to claim 98 wherein the concentration of the alkyl acrylate or alkyl methacrylate solution is about 10 to 20 percent by weight.

25 100. The product according to claim 78 wherein the film-forming layer comprises an aqueous solution of gum arabic.

101. The product according to claim 100 wherein the concentration of the gum arabic solution is about 5 to 40 percent by weight.

30 102. The method or product according to claims 1 or 52 wherein the aromatic isocyanate compound is 4,4'-diphenyl- methane diisocyanate.

103. The method or product according to claims 1 or 52 wherein the aromatic isocyanate compound is hexamethylene diisocyanate.

5

104. The method or product according to claims 1 or 52 wherein the aromatic isocyanate compound is selected from the group consisting of 4,4'-diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate, hexamethylene diisocyanate, 10 toluene diisocyanate, 0-tolidine diisocyanate, xylylene diisocyanate (XDI), hydro xylylene diisocyanate, and hydro 4,4'-diphenylmethane diisocyanate.

105. The method or product according to claims 1 or 15 52 wherein the secondary layer additionally comprises an anti-hydrolysis agent.

106. The method or product according to claim 105 wherein the anti-hydrolysis agent is a polycarbodiimide.

20

107. The method or product according to claims 1 or 52 wherein the secondary layer additionally comprises a weather-resistance agent.

25 108. The method or product according to claim 107 wherein the weather-resistance agent is {tetrakis [methylene-3-(3'5'-ditert-butyl-4'-hydroxylphenyl) propionate] methane}.

30 109. The method according to claims 1 or 28 wherein the drying conditions occur at a temperature in the range of from 50°C to 60°C.